

Engineering Switchable Rotors in Molecular Crystals with Open Porosity

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Supporting Information

ABSTRACT: The first example of a porous molecular crystal containing rotors is presented. The permanently porous crystal architecture is sustained by rotor-bearing molecular rods which are connected through charge-assisted hydrogen bonds. The rotors, as fast as 10^8 Hz at 240 K, are exposed to the crystalline channels, which absorb CO_2 and I_2 vapors at low pressure. The rotor dynamics could be switched off and on by I_2 absorption/desorption, showing remarkable change of material dynamics by the interaction with gaseous species and suggesting the use of molecular crystals in sensing and pollutant management.

The quest for molecular rotors in the solid state has intensified during the past few years, boosted by the potential of such systems in the fabrication of tunable molecular devices with unique switchable dielectric, refractive, and optoelectronic properties.¹ Such properties are influenced by the organization of the rotors, which can be regularly arranged into arrays within periodic materials.² In general, materials with fast rotor dynamics can be prepared by end-capping the rotors with bulky substituents, which realize low-density crystals and provide the free volume necessary for individual rotors to rotate. An innovative strategy has come from the use of mesoporous materials, namely organo-silicas, and of metal–organic frameworks, which provide not just the minimum space for rotation to occur, but larger and accessible free spaces.^{3,4} The use of porous materials is very stimulating, because the open porosity exposes the rotors directly to gases and to molecular species diffusing in, enabling modulation of the rotor dynamics by chemical stimuli.^{3a}

Fully organic porous materials have not yet been applied for the realization of arrays of rotors in the solid state. The fabrication of porous molecular crystals (PMCs) with permanent porosity⁵ would be attractive in this context because of the versatility of organic synthesis and the spontaneous self-assembly of the porous structure by simple crystallization, providing a platform for the design of novel low-density porous architectures. Moreover, guided by crystal engineering,⁶ interactions of variable strength can be explored to arrange molecular rotors in the designed structures. However, crystalline molecular materials with permanent porosity are relatively rare and somewhat difficult to fabricate. Therefore, our goal was twofold: (a) to

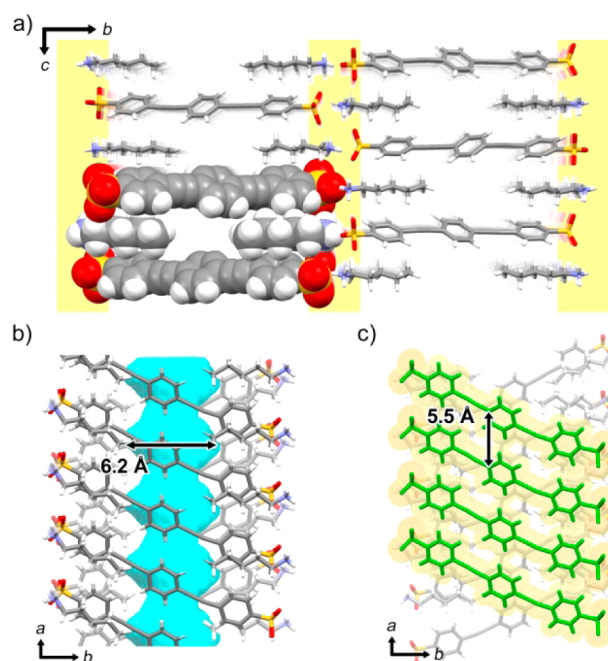


Figure 1. (a) Crystal structure of the permanently porous compound **1** as viewed along the channel axis. The yellow area represents the region containing the polar layer. (b) Empty channels as described by sky blue region calculated by a sphere of 1.0 Å. (c) SPEB moieties in the crystal structure showing the distance between the two central *p*-phenylene rings.

ensure a robust yet porous framework consolidated by intermolecular interactions and (b) to insert mobile elements operating as rotors in the molecular structure. Actually, the combined properties of open porosity and rotor dynamics have never been achieved in PMCs.

Here we present for the first time a molecular crystal that shows an extremely fast dynamics of rotors and a low-density architecture endowed with permanent porosity and capable of gas absorption. The porous and absorptive molecular structure was realized by the robustness of charge-assisted hydrogen bonds and the use of rigid molecular rods bearing the rotors. In fact, we

Received: November 12, 2013

Published: December 30, 2013

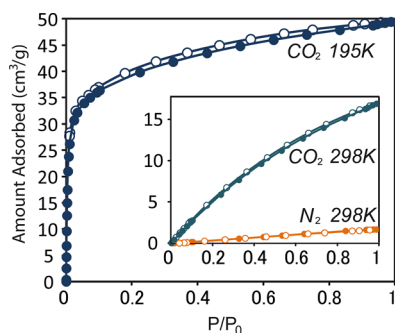


Figure 2. CO₂ adsorption and desorption isotherm at 195 K of compound **1** showing the permanent porosity of the crystalline material. Inset: CO₂ and N₂ adsorption and desorption isotherms at 298 K.

designed a suitable strut that contains a central *p*-phenylene unit (*the rotor*) connected through ethynyl groups to other *p*-phenylenes and terminated by two sulfonate anions. The strut was shown to spontaneously self-assemble with *n*-alkylammonium counterions (Figures 1 and S1).

The *p*-phenylene rotor is pivoted at the center of the rod, like a wheel mounted on an axle, and is pivoted between two triple bonds, thus experiencing a virtually barrier-free rotation. The resulting molecular building shows low-density packing wherein empty crystalline channels are self-organized. The pores are open and easily accessible from the gas phase, as proven by reversible CO₂ adsorption and iodine uptake. The rotor speed can be reduced by the molecular species diffused in the open nanochannel, but the rotation was enhanced again after guest removal under vacuum, realizing crystals which are switchable in their dynamics.

The molecular strut 4,4'-bis(sulfophenylethynyl)benzene (SPEB) was crystallized with *n*-pentylamine (PA) from a mixture of methanol and 1,4-dioxane to yield the inclusion compound with 1,4-dioxane. The porous crystalline compound **1** was obtained after evacuation under mild conditions (10⁻² Torr and 80 °C for 1 h), and its crystal structure was solved by single-crystal X-ray diffraction (monoclinic space group *P*2₁/*n*). It consists of hydrophobic layers orderly alternated with polar double-layers (Figure 1a, Table S1) forming a 2D charge-assisted hydrogen-bond network (Figure S3). The crystal structure revealed an array of parallel and independent 1D channels with average cross-section of 4.6 × 6.2 Å² to which the *p*-phenylene moieties are exposed (Figures 1b and S4). No residual electron density was detected inside the channels.

The permanent porosity with open channels of the crystalline material was demonstrated by CO₂ adsorption/desorption measurements performed at 195 K (Figure 2). It showed a type-I Langmuir profile with an uptake of 50 cm³(STP)/g at 0.8 bar, consistent with 1.4 CO₂ moles per mole of host (Figure 2) and the virtual complete filling of the available space. The uptake is competitive with that of zeolites containing 1D channels with comparable cross-section.^{5a,7,8} The isosteric heat of adsorption, according to Clausius–Clapeyron equation, was 21 kJ/mol, which is consistent with direct interaction of carbon dioxide with hydrophobic moieties such as the aromatic rotors of SPEB and aliphatic chains of PA.⁵ Conversely, nitrogen is scarcely absorbed by the microporous material, similarly to other materials of the same channel size, indicating a CO₂/N₂ selectivity ratio of 10 at room temperature and 1 bar. This is a rare example of permanently porous crystal sustained by charge-assisted H-bonding between purely organic molecules.⁹

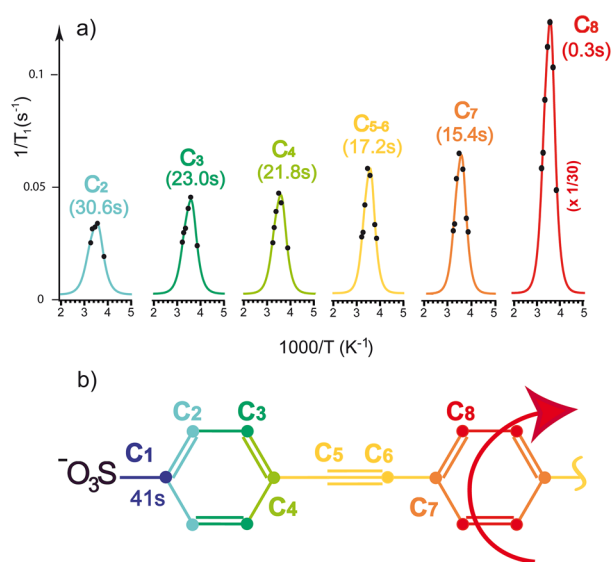


Figure 3. (a) Temperature-dependent ¹³C spin–lattice relaxation rates at 75 MHz for the carbon nuclei of SPEB moiety reporting the shortest ¹³C T₁ measured for each carbon. (b) Chemical structure of the SPEB moiety.

A careful analysis of the channel wall structure reveals that the separation between the centers of *p*-phenyl rings on adjacent molecules is of 5.5 Å (Figures 1c and S5). Considering that each aromatic ring possesses a lateral van der Waals hindrance of ca. 3.4 Å (each *p*-electron cloud accounts for 1.7 Å), a space much larger than that of a face-to-face close-packed configuration is available, suggesting these moieties may behave as rotors. This was evidenced by the following solid state NMR experiments.

¹³C CP MAS NMR spectra exhibit at low temperature two signals for the CH carbon of the central aromatic ring, corresponding to nonequivalent crystallographic sites in the unit cell, while at room temperature a single and intense signal appears, consistently with the dynamical exploration of the sites within the NMR time scale (Figure S10). Variable-temperature measurements of ¹³C spin–lattice relaxation rates enabled to establish correlation times by a nonlinear least-squares analysis according to Kubo–Tomita equation.¹⁰ The most efficient relaxation (T₁'s as short as 0.3 s), occurred at 278 K with a correlation time τ_c = 13 ns for CH carbon atoms (C₈), demonstrating the presence in the crystalline phase of fast molecular motions of the central phenyl-ring moieties about their molecular rotation axes (Figure 3). From the center of the rod-like moiety to the polar sulfonate heads, the relaxation times become considerably longer (T₁ = 15–40 s); i.e., the mobility is lowered on the end groups. In any case, the maximum relaxation rates of all the peripheral carbon nuclei still occur at the same temperature of 278 K, indicating that the relaxation of the carbons along the rod-like molecule is mediated by the rotation of the central *p*-phenylene ring and by oscillations and librations caused by this fast motion on the peripheral carbons (Figure 3).

²H solid-state NMR spectroscopy is a unique method to understand the motional trajectories, thus a deuterated compound on the *p*-phenylene moieties was prepared to study the dynamics of the central *p*-phenylene rotors (*d*₄-1). Such technique is a key method to reveal the mechanism of reorientation of the C–D vectors.¹¹ The ²H NMR spectral profiles vary progressively with increasing temperature from 193 to 295 K (Figure 4) and were simulated successfully by

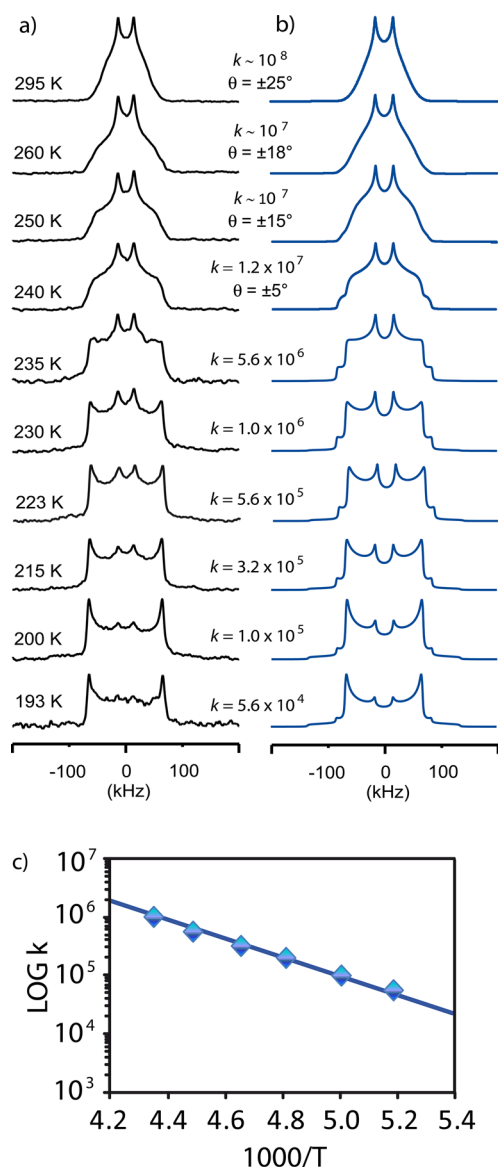


Figure 4. (a) Experimental and (b) simulated ^2H NMR spectra of porous compound $d_4\text{-1}$ as function of temperature. The ^2H NMR spectral profiles were simulated considering a two-site 180° flip mechanism. k is the 180° flip rate constant and are expressed in Hz. (c) Arrhenius plot of $\log(k)$ vs the inverse of absolute temperature.

considering reorientation rates that are intermediate ($10^3\text{--}10^7$ Hz) or fast (above 10^7 Hz) on the characteristic time scale of wide-line ^2H NMR.¹² The spectra were carefully reproduced by simulation and the line-shape analysis indicates that the mechanism of motion is consistent with a rapid two-site 180° flip reorientation of *p*-phenylene moieties about their *para*-axis. At a temperature as low as 240 K, the spectrum profile shows singularities separated by 28.1 kHz, which corresponds to one-fourth of the splitting of the *static* pattern (Pake spectrum) and a line shape typical of exchange rates $k > 10^7$ Hz. This extremely rapid regime of motion in a crystalline solid at about 240 K is quite exceptional and outperforms the exchange rates of *p*-phenylene groups in most organic materials and solid polymers.^{2,13} The *p*-phenylene dynamics discovered in this case is orders of magnitude faster than those recently observed in metal–organic frameworks, which are still in slow exchange regimes at room temperature.⁴ To the best of our knowledge this

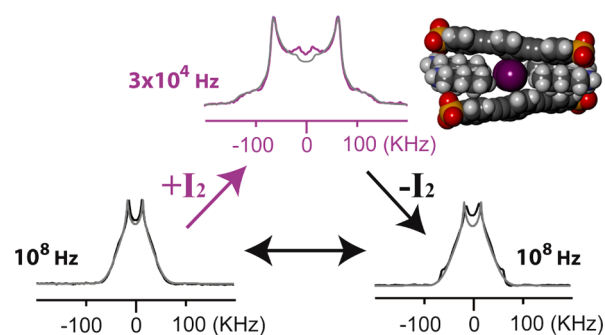


Figure 5. ^2H NMR spectra of pristine empty (left), iodine-loaded (center), and I_2 -freed sample (right) (expt, black and violet lines; calc, gray lines). The exchange rates are reported. Line broadening of 8 kHz was applied to the simulated spectrum of I_2 -loaded sample.

compound exhibits the fastest dynamics of *p*-phenylene units realized in a porous material.¹⁴ The motion in compound $d_4\text{-1}$ also persists at low temperatures and exchange rates k are still as fast as 10^5 Hz at temperatures as low as 200 K.

The energy barrier for rotation can be calculated by an Arrhenius plot, showing an activation energy $E_a = 6.7$ kcal/mol and a motional frequency extrapolated at infinite temperature $k_0 = 2.4 \times 10^{12}$ Hz (Figure 4c). This value of k_0 is consistent with the moment of inertia of the *p*-phenylene ring rotating about its main axis.¹⁵ Remarkably, the activation energy is the lowest found in porous materials with the same inertia mass and $k_0 \approx 10^{12} \text{ s}^{-1}$.^{3,4} Above 240 K, further line width reduction together with the fading of the spectral shoulders is evident, indicating that additional rapid librations of the phenylene rings about the *para* axis must be included in the dominant 180° flip mechanism, which is preserved in the robust charge-assisted hydrogen-bond network. Rates in the fast exchange limit $>10^8$ Hz and libration amplitudes up to $\theta = \pm 25^\circ$ are achieved at room temperature, also consistently with ^{13}C T_1 experiments.

Moreover, by exploiting the accessibility of the rotors from the gas phase, it is possible to regulate the rotor dynamics by the intervention of suitable species diffused into the channels. As a case study, the crystals were exposed to iodine vapors and a dramatic hampering effect was shown on rotor dynamics (Figure 5). This was revealed by ^2H NMR spectra which showed a progressive metamorphosis from an extremely *mobile* pattern to a *static* Pake spectrum ($k = 3 \times 10^4$ Hz), clearly showing that molecular iodine could enter quantitatively the crystal channels and affect by 4 orders of magnitude the rotor dynamics (the barrier for rotation was increased by 3.8 kcal/mol). Independently, ^{13}C T_1 relaxation times of the central ring carbons, which are much longer at room temperature in the I_2 -treated sample (13 s, Figure S15), confirm a considerable slow down of motion. The I_2 adsorption of compound **1** at the equilibrium with I_2 vapors amounts to 36 wt%, corresponding to a virtual complete filling of the channels. The treatment of the crystals under vacuum resulted in the reverse phenomenon and the regain of the pristine fast rotor-dynamics. In general terms, the experiment successfully showed, for the first time, that molecular rotors can be actively manipulated from the gas phase by simple exposure to vapors. The guest modulates the host dynamics, triggering the spectroscopic signal, with stimulating perspectives for sensing and molecular detection.

In conclusion, we have built a permanently porous molecular crystal containing rotors mounted in their pore walls. This unique combination of two challenging tasks of the present day

research has been successfully pursued by the rationale design of the molecular struts. Indeed, the synthesis of a rigid molecular rod, which can be clipped at the ends by organoammonium counterions forming a 2D hydrogen bond motif, allowed us to assemble a robust yet porous crystal, preventing the formation of a close packed structure. The low flexibility and axial symmetry of the molecular rod ensures a stable axle for the rotation of the central element, while the conformational softness of Csp_2-Csp pivotal bonds sustained by the ethynyl groups enabled facile rotation with frequencies as high as 10^8 Hz at room temperature. The property of permanent porosity renders the rotors massively accessible from the gas phase, opening a window for applications as sensors of adsorbates and, if mobile dipoles were inserted, of tunable dielectrics. After this seminal result, the rich possibilities offered by the organic synthesis suggest a diversity of perspectives, enabling the engineering of dynamically active crystals. Thus, for instance, the potential of growing large molecular crystals in organic media allows the rotor arrays to be macroscopically oriented and integrated in properly engineered devices.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by PRIN 2011 (Italian Ministry of Education) and Cariplo Foundation (Milano, Italy) 2012-0921. A.Y. was supported by JSPS and Grant-in-Aids for Scientific Research on Innovative Areas (area 2107, No. 24108723). A.Y. thanks the Research fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists for financial support. N.T. acknowledges Grant-in-Aids for Scientific Research on Innovative Areas "Coordination Programming" (area 2107, No. 24108723) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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